(12) UK Patent Application (19) GB (11) 2 109 265 A

(21) Application No 8233066
(22) Date of filing 19 Nov 1982
(30) Priority data
(31) 3146142
(32) 21 Nov 1981
(33) Fed. Rep of Germany (DE)
(43) Application published
2 Jun 1983
(51) INT CL³
B01J 10/00
C07C 67/00
(52) Domestic classification
B1F 4F
B1B E
B1R 201 M1
C2C 200 20Y 218 231 240
30Y 360 361 362 366 368
36Y 37X 491 623 628 633
638 648 CB CK CY PJ
U1S 1519 B1B B1F B1R
C2C
(56) Documents cited
GB 1211783
EP A1 0021594
(58) Field of search
B1B
B1F
B1R
(71) Applicants
Henkel KGaA,
(FR Germany),
Postfach 1100,
D-4000 Dusseldorf 1,
Federal Republic of
Germany.
(72) Inventors
Norbert Bremus,
Lutz Jeromin,
Eberhard Peukert.
(74) Agent and/or Address for
Service
Elkington and Fife,
High Holborn House,
52/54 High Holborn,
London WC1V 6SH.

(54) **Reaction column and use thereof**

(57) A low vapour load reaction column comprises one or more bubble plates 1 with immersion caps 2 of which the side edges comprise openings or perforations 3 for the passage of the gas phase, one or more immersed inlets 5, one or more outlets 7 and, optionally, inflow and outflow weirs 6, 8, characterised in that it has an internal diameter of from 500 to 3000 mm and one or more orifices (4) below each bubble cap (2) of which the openings in the plate (1) are designed in such a way that the dry pressure loss occurring under the particular conditions under which the column is operated are 15 times to 60 times greater than the pressure difference between the pressure of the liquid column at the outlet and the pressure of the liquid column at the inlet.

This column is particularly suitable for the continuous catalytic esterification of aliphatic carboxylic acids of 2 to 24 carbon atoms with alcohols in countercurrent, and for transesterifications.

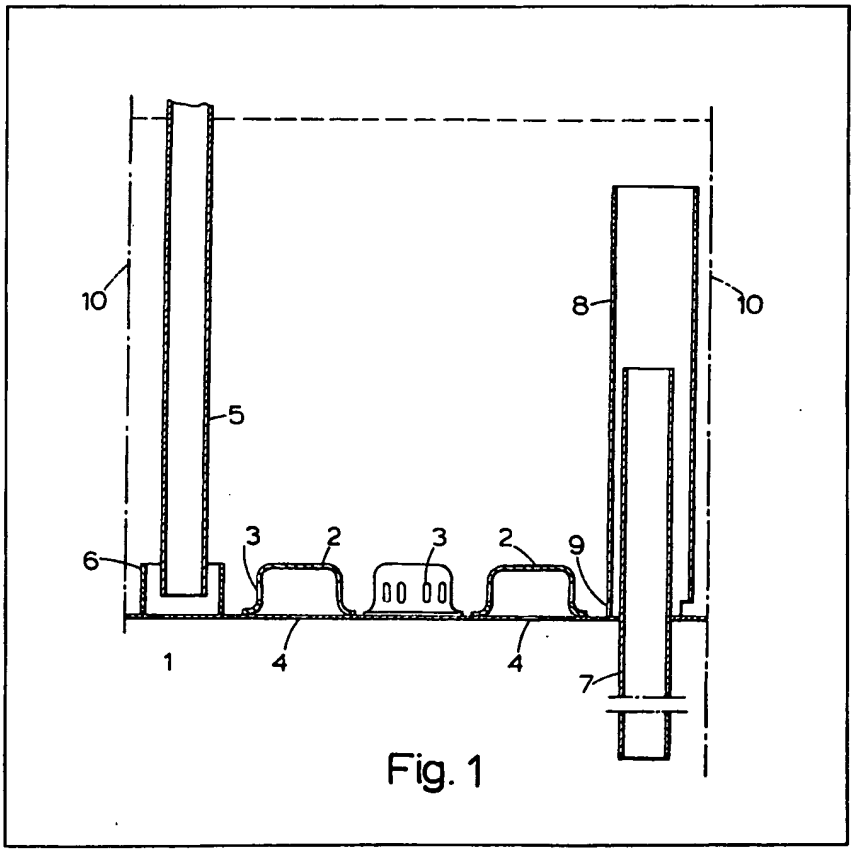

Fig. 1

GB 2 109 265 A

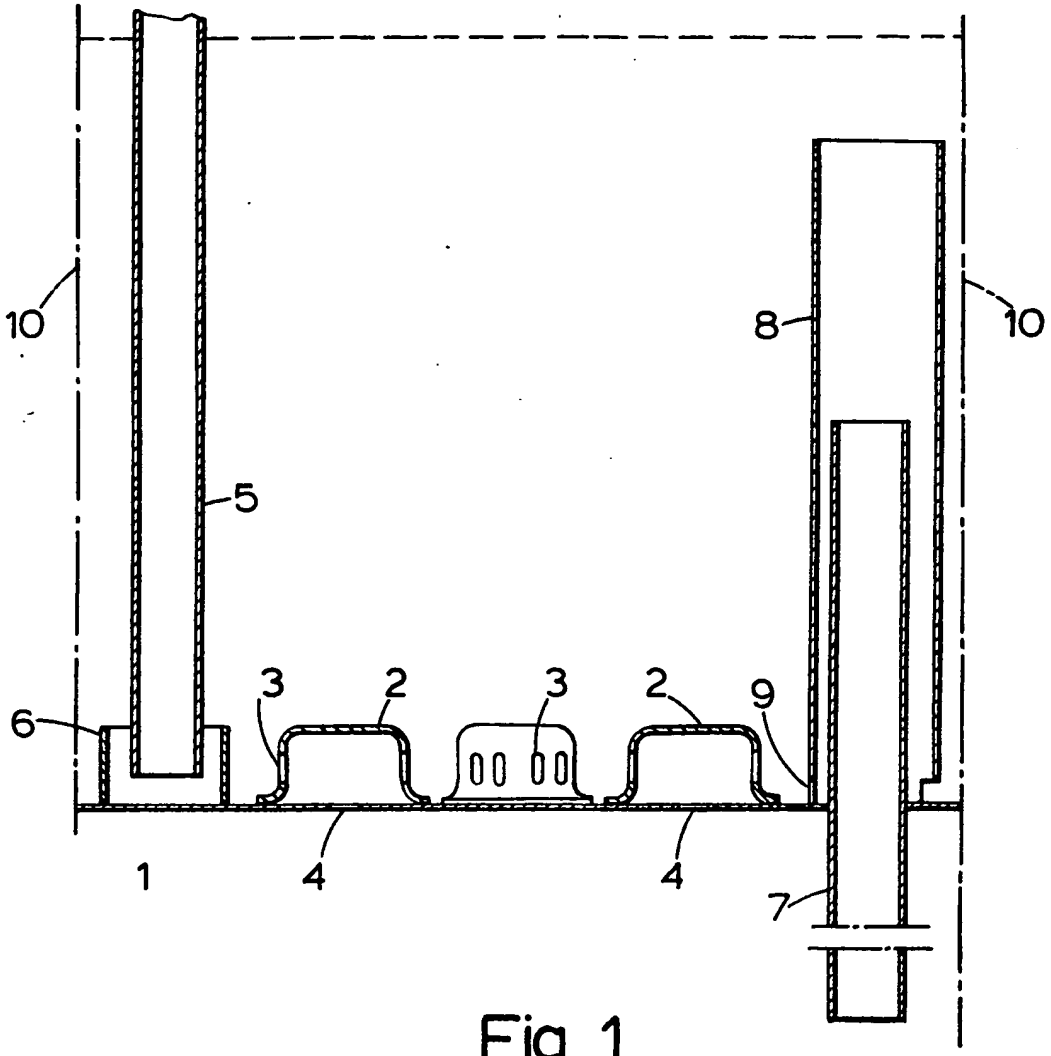

Fig. 1

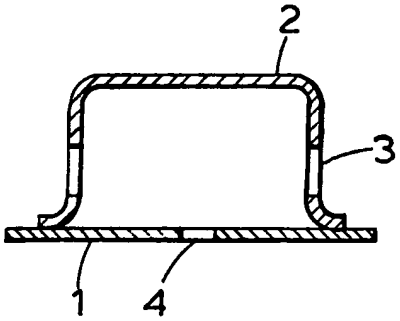

Fig. 2

2109265

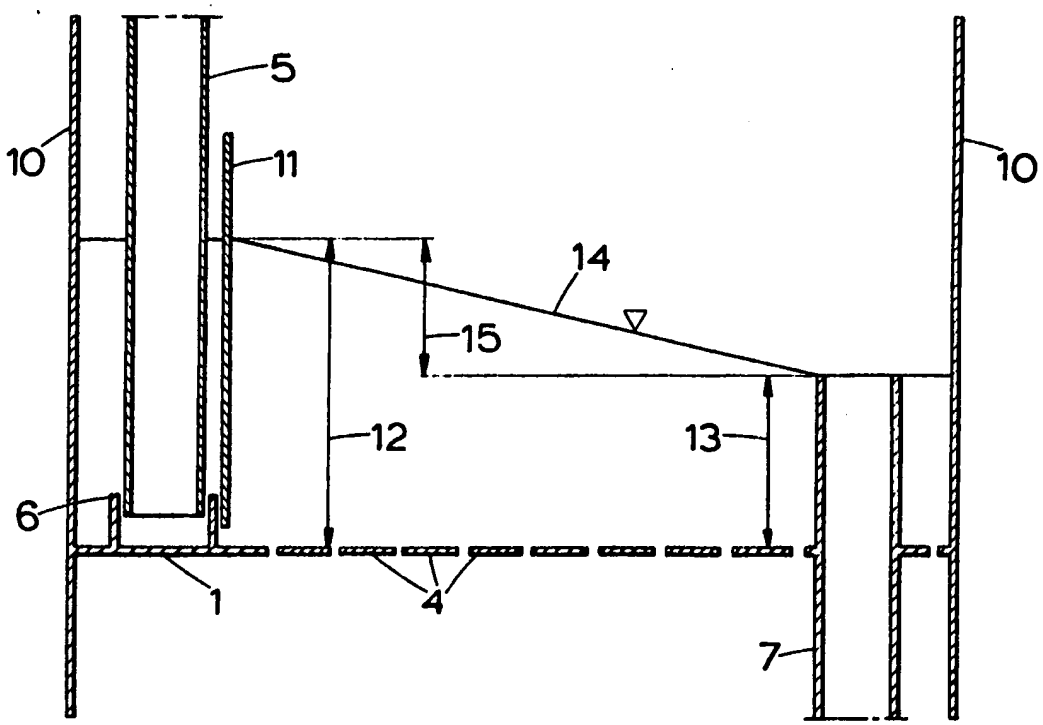

Fig . 3

SPECIFICATION

Reaction column and use thereof

This invention relates to a reaction column and to the use thereof; more particularly, it relates to a low vapour load reaction column comprising one or more bubble plates with immersion caps of which the side edges comprise openings or perforations for the passage of the gaseous phase, one or more submerged inlets, one or more outlets and, optionally, inflow and outflow weirs.

The column according to the present invention may be used for a variety of reactions characterised by a low vapour load in the column. More particularly, however, the present invention also relates to the use of such a reaction column for the continuous catalytic esterification of carboxylic acids with alcohols.

Columns comprising one or more bubble plates have been known for decades and are widely used.

An essential feature of these bubble plates is that the opening present in the column plate over which the bubble cap is arranged has substantially the same cross-section as the bubble cap arranged there over. This may also be defined to the effect that the vapour neck cross-section, the annular gap between the vapour neck and the bubble cap and the sum of the vapour outlet slots occupy substantially the same surface area.

These bubble plates cannot be used for reactions and/or mass transfers in the column where only low vapour loads and, at the same time, high liquid levels (weir height) are present because liquid would weep through them. Such problems arise, for example, in processes for the continuous catalytic esterification of, in particular, fatty acids of the type described in DE-AS No. 2,503,195, and also in transesterification reactions, for example of carboxylic acid methyl esters with isopropanol, or in the esterification of glycerol with acetic acid to form glycerol triacetate.

In the context of the present invention, the expression "low vapour loads" is to be understood to mean vapour loads which are lower by a factor of from 5 to 20, preferably from 10 to 15, then the normal lower vapour loads on rectification plates. In practice, therefore, the vapour loads in question, expressed by the comparable air velocity, based on the free column cross-section, are from 0.05 to 0.3 m/s, preferably from 0.07 to 0.02 m/s.

For solving these problems, DE-AS No. 2,503,195 proposes an apparatus in which the inner bubble cap of double bubble plate columns is provided with a bore. However, this construction has proved to be relatively complicated. In addition, it may give rise to blockages if, when the column is in use, any products present in small quantities in the inflowing streams accumulate in the column and build up in the relatively narrow gaps between the two bubble caps. This is the case, for example, with certain cracking products which, in the esterification of fatty acids with alcohols, may be introduced into the column with the superheated alcohol vapours. The double bubble cap may become clogged, thus blocking the column.

An object of the present invention is to provide a column which has a simple construction and which, at least for the most part, does not have the disadvantages referred to above and in the use of which the problems mentioned above are at least largely avoided.

Accordingly, the present invention relates to a low vapour load reaction column comprising one or more bubble plates with immersion caps of which the side edges comprise openings or perforations for the passage of the gaseous phase, one or more submerged inlets one or more outlets and, optionally, inflow and outflow weirs, characterised in that the column has an internal diameter of from 500 to 3000 mm and one or more orifices (4) below each bubble cap (2) of which the openings in the plate (1) are designed in such a way that the dry pressure loss occurring under the particular conditions under which the column is operated is at least 15 times and at most 60 times greater than the pressure difference between the pressure of the liquid column (13) at the outlet and the pressure of the liquid column (12) at the inlet.

As mentioned above, the reaction column according to the present invention may be used for a variety of reactions, as will be illustrated below.

However, the column according to the present invention may be used with particular advantage for the continuous catalytic esterification of fatty acids with alcohols in countercurrent in the liquid phase, as described in DE-AS No. 2,503,195.

The immersion caps of the column according to the present invention correspond to the prior art and have the conventional openings or perforations for the passage of the gas phase. The total surface area occupied by the bubble caps on one plate preferably amounts to from 5 to 40 %, based on the free volume cross-section minus the surface area occupied by the inlet and outlet. As in the prior art, the column generally contains at least 5 plates. Industrial columns generally contain at least 20, preferably at least 25, plates. The upper limit may amount to 100 plates, preferably to 80 plates.

The ratio between the vapour throughflow area through the bubble caps mounted on a plate to the free column cross-section is preferably from 0.3 to 6 %, preferably from 2 to 5 %. This preferably distributed over at least four openings or perforations per bubble cap for the passage of the gas phase. In industrial bubble caps, there are from 10 to 20, preferably from 12 to 18, opening or perforations per bubble cap.

These openings preferably have a diameter of from 2 to 5 mm or are in the form of slots which are uniformly distributed around the circumference and which have a cross-section substantially corresponding to the cross-section of the above-mentioned bores. The bores are preferably situated at a height of from 5 to 10 mm above the plate, slots generally begin at the lower edge of the bubble cap or from 3 to 10 mm above it.

An essential feature of the present invention is that the plates are from 500 to 3000 mm in diameter. With plates having a smaller diameter, the problems mentioned above are not encountered to a particularly serious extent. Plates having larger diameters are hardly used in practice. The lower limit is preferably at about 800 mm, more preferably at about 900 mm. The upper limit to the diameter is determined in practice by the strength of the constituent material of the column walls and, in view of the current column throughputs, is generally at about 2000 mm, preferably at 1700 mm, more preferably at 1500 mm.

Each plate comprises one or more submerged inlets, one or more outlets, optionally inflow and outflow weirs and, optionally, heating systems. In practice, liquid levels of from 80 to 500 mm, preferably at least 100 mm, more preferably at least 120 mm, above the height of the outflow weir are generally used in practice. The upper limit to the liquid level is generally at 400 mm, preferably at about 300 mm, more preferably at about 200 mm.

When columns of the type in question are in operation, a liquid gradient develops between the inlet (optional inflow weir) and outlet (optional outflow weir). This depends on numerous parameters, including, for example, the density of the liquid, the viscosity of the liquid and the liquid load (volume flow based on the width of the weir). In every case, however, the liquid gradient is a measurable value spontaneously adjusted during the operation of a column under given conditions. The effect of this liquid gradient is that the liquid level is higher at the inlet than at the outlet. In columns of the type described above, the difference in the liquid level at the inlet and outlet is of such a magnitude that a difference in the hydraulic pressure of from 0.1 to 2, preferably from 0.5 to 1.5, mbar per metre of distance between the inlet and outlet is adjusted on the plate. This difference in pressure may be measured as follows: the column is operated with closed bubble caps in regard to the liquid load under conditions under which the reaction or mass transfer is to be carried out. In the interests of simplicity, the apparatus used for this purpose is a model plate which corresponds to the plates in the column actually used and which is operated at ambient temperature and pressure, i.e. at about 25°C/atmospheric pressure, being open upwards so that the liquid level may readily measured at the places mentioned. Accordingly, since the measurement is not carried out in regard to temperature and pressure under the conditions under which the column will later be operated in the particular case in question, the model test has to be carried out using liquids and liquid loads which are calculated using the theory of similarity (mainly Reynolds' analogy) from the operating conditions prevailing during the subsequent proposed operation of the column. In this connection, it may be necessary to use temperatures other than ambient temperature and liquids other than water in the model test. So far as the practical needs of the present invention are concerned, the value thus determined corresponds to the value subsequently occurring in the actual operation of the column. However, it is also possible to install suitable devices for measuring the liquid levels at the places mentioned in the technical column as actually operated.

Another essential feature of the present invention is that, beneath each bubble cap, there are orifices which bring about a so-called "dry pressure loss" as the liquid flows through the plate. This dry pressure loss may be measured as follows: in a model plate of the type described above, the outlet pipe is blocked. An air mass is forced downwards through the model plate at a comparable air velocity such as corresponds to the vapour load during operation of the column. No liquid is present on the plate. The pressure difference between the air pressure immediately below and immediately above the plate is the dry pressure loss. In this model test, too, the dry pressure loss thus determined corresponds with sufficient accuracy to the pressure loss occurring in the actual operational state of the column.

Another essential feature of the present invention is that this dry pressure loss must be from 15 to 60 times greater than the hydraulic pressure difference attributable to the pressure gradient.

Column plates having various orifices are tested in this way and the size of the orifices relevant to the particular application is determined. By series measurements, it is possible to draw graphs with the parameters in question so that there is then no need for future measurements. In that case, the appropriate orifice diameter for a desired application may be determined from so-called "pressure loss characteristics".

The dry pressure loss preferably amounts to at least 20 times, more preferably at least 25 times, the above-mentioned hydraulic pressure difference. The maximum dry pressure loss preferably amounts to 50 times, more preferably 35 times, the hydraulic pressure difference. At all events, the dry pressure loss has to be selected in such a way that liquid is prevented from weeping through the column in any part thereof. In some reactions or mass transfer processes, however, the vapour load at the head of the column may differ considerably from that in the lower part of the column due to the diffent average molecular weights of the substances present in the vapour phase. In such cases, it may be necessary for the orifices in the upper part of the column to differ in size from those in the lower part of the column to prevent liquid from weeping through the column in all parts thereof. For reasons of energy, the dry pressure loss should be kept as low as possible, although it should, of course, be high enough to prevent liquid from weeping through the plates.

The shape of the cross-section of the orifices may vary within wide limits. In order to simplify production, circular bores are generally advisable. However, it is also possible to use other geometric forms, for example squares or rectangles, for the openings.

It is extremely surprising that, by virtue of this remarkably simple construction, esterification reations, for example, may be carried out with high volume/time yields without disturbances in the operation of the column or without liquid weeping through the column. By virtue of the simpler construction, the costs involved in the production of a plate according to the present invention are, of course, considerably lower than those involved in the construction of plates of the type described in DE-AS No. 2,503,195 mentioned

above.

The present invention also relates to the use of the above-described column for the continuous catalytic esterification of aliphatic carboxylic acids containing from 2 to 24 carbon atoms with alcohols in countercurrent in the liquid phase. In one embodiment, aliphatic carboxylic acids containing from 2 to 6, preferably from 2 to 4, carbon atoms may be esterified with aliphatic alcohols containing from 2 to 4 hydroxyl groups. One particularly important technical example of this is the esterification of acetic acid with glycerol. In another embodiment, fatty acids containing from 6 to 24 carbon atoms are esterified with aliphatic monohydric alcohols containing from 1 to 6 carbon atoms. The esterification reaction in question is of the type normally encountered in the chemistry of fats. Examples of fatty acids of the type in question are tallow fatty acids, coconut oil fatty acids, soya oil fatty acids, palm oil fatty acids and other fatty acids and their mixtures of vegetable and animal origin. Methanol, ethanol, *n*- and iso-propanol, *n*-butanol and, optionally, the isomers have acquired particular technical significance as alcohols.

The column according to the present invention may also be used for transesterification reactions, for example of myristic acid methyl ester with isopropanol to form isopropyl myristate. Further examples of transesterification reactions include the transesterification of animal and vegetable fats and oils with the lower alcohols mentioned above to form the corresponding esters.

The column may also be used for the absorption of certain compounds from gas mixtures on suitable (washing) liquids, for example the absorption of sulphur dioxide into alkaline washing liquids.

Referring to the accompanying drawings:

Figure 1 illustrates a longitudinal section through a plate of the reaction column.

Figure 2 illustrates a longitudinal section through a bubble cap.

Figure 3 is a basic diagram illustrating the principle of measurement of the hydraulic pressure difference.

As shown in Figure 1, bubble caps 2 are arranged on the plate 1, comprising vapour throughflow openings in the form of slots 3 distributed around the circumference thereof. Below the bubble caps are orifices 4. The inlet pipe 5 is immersed in an immersion bowl 6. In this case, the immersion bowl 6 acts as an inflow weir. However, a special used inflow weir may be arranged in known manner between the immersion bowl 6 and the first bubble cap, although this is not shown in the drawing. Arranged around the outlet pipe 7 is an outflow weir 8 which, in this particular case, is constructed in such a way that it concentrically surrounds the outflow pipe and affords protection against spray. Openings 9 for the passage of the liquid are arranged in the lower part of the outflow weir 8. The liquid level in the outflow pipe 7 is determined by the height thereof. In practice, the immersion bowl 6 also comprises opening for possible emptying during startup of the column, although in the interests of simplicity these openings are not shown in the drawing. The wall of the column is represented by the dotted line 10.

In Figure 2, the same reference numerals have been used for denoting the same components.

Measurement of the pressure difference will now be described with reference to Figure 3. The column plate 1 has only been diagrammatically illustrated, i.e. the bubble plates situated thereon have not been shown. Only the orifices 4 are shown. The arrangement comprises an inlet pipe 5 with an immersion bowl 6 and an outlet pipe 7. An inflow weir 11 is arranged on the inflow pipe. In the interests of clarity, an outflow weir has not been shown on the outflow pipe. The liquid level 12 at the inflow weir is higher than the liquid level 13 at the outflow pipe. Accordingly, the liquid level 14 shows a gradient and the difference between the liquid level 12 and the liquid level 13 is denoted by reference 15. The pressure difference between the pressure of the column of liquid at the outlet and the pressure of the column of liquid at the inflow weir may be worked out from this difference between the respective liquid levels. In the absence of an inflow weir 11, the liquid level has to be directly measured at the inlet pipe 5. In the presence of an outflow weir, the converse applies.

The following Examples illustrate the present invention:

Example 1

An esterification process is carried out using a reaction column comprising 32 plates, in which the upper 15 plates are heatable by tubular coils on the plates, and having a height of 11 metres, a plate diameter of 1100 mm, 70 bubbles caps per plate, an inlet and an outlet and an inflow weir and an outflow weir, the height of the outflow weir being 150 mm and the distance between the inflow and outflow weirs amounting to 785 mm. The surface area occupied by the bubble caps on a plate amounts to 17 % of the surface area of the plate between the two weirs; this ratio of the vapour throughflow area (slots) through the bubble caps arranged on a plate, based on the free cross-section of the column, amounts to 3.5 %. If 3960 kg/h of a tallow fatty acid mixture (acid No. 200) containing a conventional catalyst is delivered to the uppermost plate of the column at a temperature of 250°C and if a mass flow of methanol gas of 1040 kg/h is fed in below the lowermost plate again at a temperature of 250°C under a pressure in the column of 11 bars, methyl esters having an acid No. below 0.5 are obtained in the sump of the column in a quantity corresponding to the fatty acid, while a gaseous water-methanol mixture corresponding to the reaction and to the excess of methanol is obtained at the head of the column. The liquid gradient determined with water using a model plate in the original size in a plate test stand amounts to 0.13 mbar/m. The orifices were selected in such a way that the dry pressure loss amounts to 30 times the pressure difference between the inflow and outflow weir on the basis of the measured liquid gradient. With the geometric form of a circular orifice, the diameter of these orifices amounts to 10 mm. The effect of the described choice of the size of the orifices is that the column functions

satisfactorily, i.e. no liquid weeps through either at the head or at the lower end of the column.

Example 2

Using a reaction column comprising 35 plates of the type described in Example 1 and having a height of 16 metres, a plate diameter of 1.1 m and an outflow weir height of 150 mm, a conversion of 90 % is obtained in the esterification of glycerol with acetic acid, based on the glycerol used. To this end, 440 kg/h of glycerol are delivered to the uppermost plate with a conventional catalyst at a temperature of 140°C, while 570 kg/h of acetic acid in gaseous form are delivered to the lowermost plate at a temperature of 150°C. The column has a sump pressure which is only slightly above ambient pressure. While 94 % of the water of reaction is removed in gaseous form substantially free from acetic acid at the head of the column thus operated, up to 90 % of reacted glycerol may be removed at the sump of the column in the form of glycerol acetate mixed with excess acetic acid and approximately 6 % of the water of reaction. The liquid gradient for glycerol under the operating conditions amounts to 0.16 mbar/m. 25 times the hydraulic pressure difference between the inflow and outflow weirs was regarded as sufficient both on the basis of the measured liquid gradient for the dry pressure loss of the plate and on the basis of a comparable air velocity higher in relation to Example 1, based on the free cross-section of the column. For the indicated gas load, the dry pressure loss of 3.1 mbar is obtained with a circular orifice 11 mm in diameter below each bubble cap. The effect of the described choice of the size of the orifices is that the column operates satisfactorily, i.e. no liquid weeps through either at the head or in the lower part of the column.

Standard bubble caps 50 mm in diameter (50 mm standard bubble caps) are used in the Examples. If bubble caps having a larger diameter were to be used, fewer would be required for the same column diameter. If an 80 mm diameter bubble cap were to be used instead of the standard 50 mm bubble cap, the number of bubble caps would be reduced to 60. The same flow conditions beneath the bubble cap would require a 12 mm diameter orifice. If a 125 mm diameter bubble cap were to be used, the number of bubble caps would be reduced to 30 and the orifice would have to have a diameter of 17 mm.

The surface-area ratios between the projection surface of the bubble cap and the orifice area, which are not constant, may be calculated in accordance with the following formula given certain simplifications:

$$d_2 = \frac{n_1 \cdot d_1}{n_2}$$

d_1 : orifice diameter where the bubble cap of type 1 is used.

d_2 : orifice diameter where the bubble cap of type 2 is used

n_1, n_2 : number of bubble caps then accommodated on a plate of certain diameter.

CLAIMS

1. A low vapour load reaction column which comprises one or more bubble plates having immersion caps the edges of which comprise a plurality of openings or perforations for the throughflow of a gas phase, one or more immersed inlets, one or more outlets and, optionally, inflow and outflow weirs, the column having an internal diameter of from 500 to 3000 mm and one or more orifices below each bubble cap of which the openings in the plate are such that the dry pressure loss occurring under the operating conditions is from 15 to 60 times greater than the pressure difference between the pressure of the liquid column at the outlet and the pressure of the liquid column at the inlet.

2. A reaction column as claimed in claim 1 substantially as herein described with particular reference to the Examples and/or the accompanying drawings.

3. A process for the catalytic esterification of an aliphatic carboxylic acid containing from 2 to 24 carbon atoms with an alcohol in countercurrent in the liquid phase which is carried out using a column as claimed in claim 1 or claim 2.

4. A process as claimed in claim 3 wherein an aliphatic carboxylic acid containing from 2 to 6 carbon atoms is esterified with an aliphatic alcohol containing from 2 to 4 hydroxyl groups.

5. A process as claimed in claim 4 wherein the aliphatic carboxylic acid contains from 2 to 4 carbon atoms.

6. A process as claimed in claim 4 or claim 5 wherein acetic acid is esterified with glycerol.

7. A process as claimed in claim 3 wherein a fatty acid containing from 6 to 24 carbon atoms is esterified with an aliphatic monohydric alcohol containing from 1 to 6 carbon atoms.

8. A process as claimed in any of claims 3 to 7 substantially as herein described with particular reference to the Examples and/or the accompanying drawings.

9. The use of a reaction column as claimed in claim 1 or claim 2 for effecting chemical and/or physical process.

Printed for Her Majesty's Stationery Office, by Croydon Printing Company Limited, Croydon, Surrey, 1983.
Published by The Patent Office, 25 Southampton Buildings, London, WC2A 1AY, from which copies may be obtained.